Steady-state thermally annealed GaAs with room-temperature-implanted Si

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Semi-insulating Cr-doped single-crystal GaAs samples were implanted at room temperature with 300-keV Si ions in the dose range of $(0.17–2.0)\times 10^{15}$ cm^{-2} and were subsequently steady-state annealed at 900 and 950 °C for 30 min in a H_2 ambient with a Si_3N_4 coating. Differential Hall measurements showed that an upper threshold of about 2×10^{18}/cm^3 exists for the free-electron concentration. The as-implanted atomic-Si profile measured by SIMS follows the theoretical prediction, but is altered during annealing. The Cr distribution also changes, and a band of dislocation loops ~2–3 kÅ wide is revealed by cross-sectional TEM at a mean depth of $R_p \sim 3$ kÅ. Incomplete electrical activation of the Si is shown to be the primary cause for the effect.

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To achieve electron concentrations of the order of 10^{18} cm^{-3} or higher by ion implantation for good ohmic contacts, Si has the advantage over S, Se, or Te that the implantation can be performed on samples held at room temperature, rather than at 150–300 °C.[1–3] A maximum free-electron concentration of $\sim 2\times 10^{18}$ cm^{-3} has been reported after furnace annealing at 900 °C for 30 min in a H_2 ambient and use of a sputtered Si_3N_4 cap.[1] The distribution of the free-electron concentration with depth was nearly flat and deeper than the theoretically calculated Si distribution, and the apparent overall electrical activation of the implanted Si was low ($\lesssim 20\%$) for the doses required ($\sim 10^{15}$ cm^{-2}) to reach the maximum electron concentration. We report here on experiments that establish that this effect is due to partial electrical activation of redistributed Si.

Semi-insulating <100> wafers of Cr-doped GaAs were implanted at room temperature with 300-keV Si ions to doses of 10^{14}–2×10^{15} cm^{-2}, and at about 10° from normal incidence to minimize channeling. The samples were then encapsulated with sputtered silicon nitride (~2000 Å thick) and annealed for 30 min in a hydrogen atmosphere at 800, 850, 900, or 950 °C. After the silicon nitride film was removed, Au-Ge/Pt dots were evaporated and alloyed for Van der Pauw measurements to obtain the depth profile of the free electrons and the Hall mobility by the differential stripping method.[4] Atomic depth profiles of Si and Cr were obtained by SIMS using positive-ion spectroscopy and oxygen-ion bombardment. The depth scale was derived from a mechanical measurement of the final crater depth with a Dektak, assuming a constant sputtering rate. The absolute calibration of the Si and Cr atomic concentrations was made against external standards. Transmission electron micrographs in "plan" and 90° "cross-sectional" view were obtained by chemical jet etching of standard samples and by ion milling of laterally mounted samples, respectively, as described elsewhere.[5] All data described here refer to the same sample implanted at a dose of 1×10^{15} cm^{-2} and annealed at 900 °C. Samples with approximately two times lower or higher doses or annealed at 850 or 950 °C all yielded very similar electron concentration profiles.

Figure 1 shows the measured concentrations of the im-

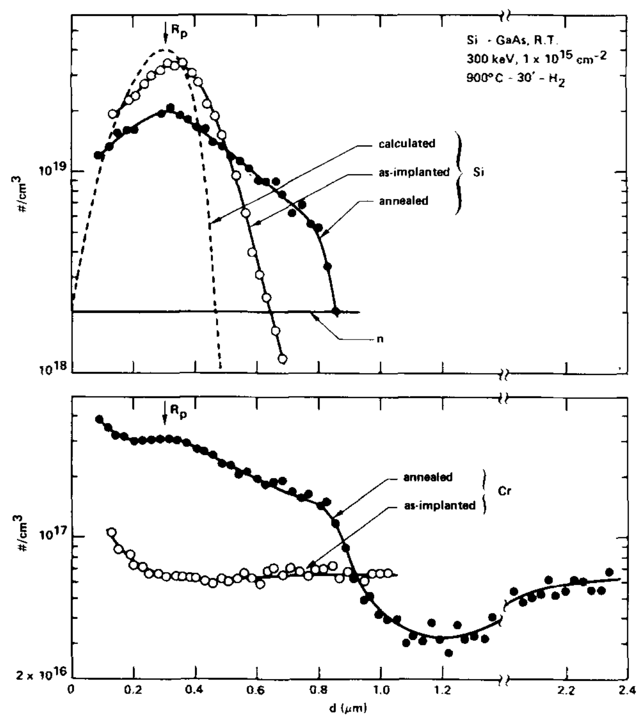

FIG. 1. Concentration profiles of Si and of Cr measured by SIMS after room-temperature implantation of Si into semi-insulating (Cr doped) GaAs before (○) and after thermal annealing (●) in a H_2 atmosphere with a sputtered silicon nitride cap. The dashed line is a calculated theoretical distribution for a dose of 10^{15} cm^{-2} Si ions of 300 keV. The straight line for the free-electron concentration n is that shown in Fig. 3.

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planted atomic Si and Cr as a function of depth below the surface before and after annealing. Also shown is the calculated profile of the as-implanted Si (dashed line) obtained with LSS range parameters by using the Pearson distribution.[6,7] This distribution agrees well with the experimentally determined Si profile in a sample implanted at liquid-nitrogen temperature. The as-implanted Si distribution is slightly broader than the calculated profile, but after the steady-state thermal annealing, the Si distribution has broadened considerably. The integral of the atomic-Si profile before annealing equals that after annealing within 5%, indicating that there is no significant loss of Si during annealing. The straight solid line in Fig. 1 refers to the measured concentration profile of free electrons reported in Fig. 3. Compared to the atomic-Si distribution after annealing, the electron concentration is lower by nearly a decade and approximately constant in value over the whole measured depth. (Beyond about 0.9 μm, the concentration of electrons exceeds that of the atomic Si, but by a magnitude which is insignificant in comparison with the uncertainties in the data for both the ordinates and the abscissas of the two plots.) Differential Hall effect measurements on other samples implanted at doses ranging from 0.17 to 2.0×10^{15} Si/cm^2 established that the electron distribution is always nearly flat and about 2×10^{18} cm^{-3} in value after annealings of 900 and 950 °C. The existence of a free-electron concentration threshold at about 2×10^{18} cm^{-3} observed previously[8] is thus confirmed. Figure 1 also shows that the atomic concentration of the Cr after annealing is enhanced in the implanted as compared to the unimplanted region. A similar result has recently been reported by Evans *et al.*[9] who investigated the redistribution of Cr after steady-state annealing in Se-implanted GaAs. They found that Cr accumulates in the implanted region. The Cr distribution peaked roughly at a depth equal to the sum of the projected range R_p and the range straggling ΔR_p of the implanted Se. We find that the Cr piles up over, roughly, the region where the Si broadens, but the two depth dependences differ noticeably. The Si profile after annealing has a maximum at R_p of the implanted Si, while Cr rises toward the surface and is constant over part of the depth.

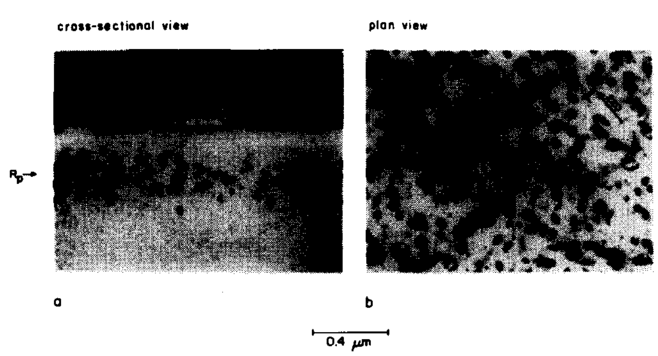

FIG. 2. Transmission electron micrographs obtained on the same sample as in Figs. 1 and 3 after thermal annealing in 90° "cross-sectional" view (a) and in "plan" view (b), using a (220)-type reflection and the strong-beam bright-field method. The dislocation loops form a band at a depth approximately equal to the projected range R_p.

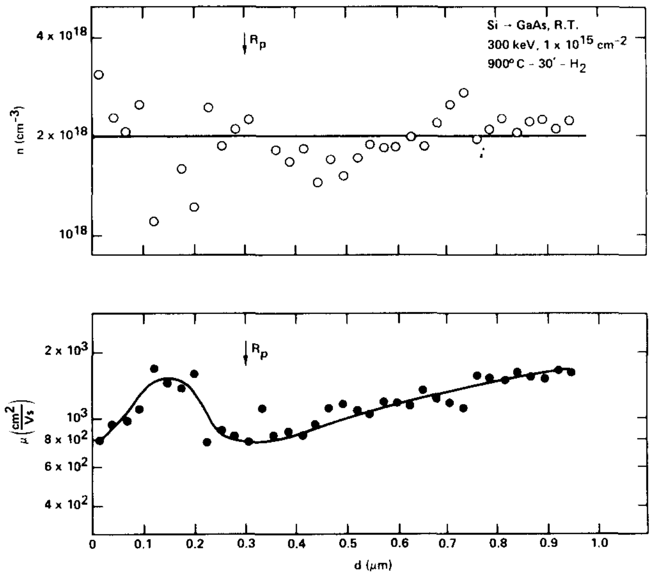

FIG. 3. Profiles of the free-electron concentration (top) and the electron Hall mobility (bottom) measured after thermal annealing on the same sample as in Figs. 1 and 2.

Two transmission electron micrographs obtained from the same samples as in Fig. 1 are shown in Fig. 2. The micrographs were taken at 100 keV and by tilting the specimen to a (220)-type reflection using the strong-beam bright-field method. The 90° cross-sectional view [Fig. 2(a)] reveals the presence of a buried band of dislocation loops 2–3 kÅ wide located at a mean depth of R_p [3 kÅ (Refs. 6,7)]. The plan view [Fig. 2(b)] shows that these loops have diameters in the range 100–1000 Å and a total density of $\sim 10^8$/cm^2. The analysis of these defects showed that the loops lay on all six-inclined {110} and four-inclined {111} planes. The presence of such loops in annealed Se$^+$- and Zn$^+$-implanted GaAs has been reported previously.[10,11] The corresponding cross-sectional and plan view micrographs of the as-implanted sample showed no visible damage in the implanted region. (The term "visible damage" refers to the damage visible by TEM.) Dislocation loops thus seem to be a standard residual defect after high-temperature furnace annealing and appear to cause the accumulation of Cr near R_p.

The results of the Hall effect measurements are shown in Fig. 3. The concentration of free electrons is roughly constant over the whole measured range and equal to about 2×10^{18} cm^{-3}. In contrast, the mobility has a dip in the vicinity of R_p. We believe that this dip is mainly due to the presence of residual visible damage in that region (see Fig. 2).

The facts presented here demonstrated that the free-electron threshold of 2×10^{18} cm^{-3} is not due to a reduction of the implanted-Si concentration to that value by diffusive spread. The measurements of the atomic Si and Cr distributions, and the observed structural defects provide insight into possible mechanisms that set up this threshold. One hypothesis is that above a threshold concentration, Si is mainly present in electrically inactive states, such as Si_{Ga}-Si_{As} neutral neighbor pairs,[12] neutral sites, or clusters. Another possibility is that Si is predominantly active, but that the Cr enhancement is responsible for additional compensation. An attempt to detect Si in either form by IR absorption spectroscopy failed, the sensitivity of the technique being marginal for individual Si substitutionals and insufficient by 10^3 for Si_{Ga}-Si_{As} pairs. We believe that the simultaneous presence of a band of residual defects, of a non-Gaussian Si distribution and of a strong Cr enhancement points toward a complex interaction between defects and the impurities during annealing. Yet the nearly constant profile of the free-electron distribution suggests a simple cause for the setting of a threshold. The hypothesis of Si_{Ga}-Si_{As} pair production is most compatible with this observation since pair formation is expected to occur at high Si concentrations.[13,14] Experiments are presently underway to investigate the effects of Si and Cr separately.

In summary, we establish the existence of a free-electron concentration threshold at 2×10^{18} cm^{-3} for Si implanted at room temperature into semi-insulating GaAs at doses $\gtrsim 0.2\times 10^{15}$ cm^{-2}, after annealing under steady-state conditions at 900 °C or above for 30 min in a H_2 atmosphere. Both Si and Cr undergo major redistribution during annealing. A band of dislocations remains at a depth of about R_p. The threshold is due to incomplete electrical activation of the Si, not to a reduction of the Si to the threshold value.

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[1]J.L. Tandon, M.-A. Nicolet, and F.H. Eisen, Appl. Phys. Lett. **34**, 165 (1979).
[2]K. Gamo, T. Inada, S. Krekeler, J.W. Mayer, F.H. Eisen, and B.M. Welch, Solid State Electron. **20**, 213 (1977).
[3]F.H. Eisen, B.M. Welch, H. Müller, K. Gamo, T. Inada, and J.W. Mayer, Solid State Electron. **20**, 219 (1977).
[4]H. Müller, F.H. Eisen, and J.W. Mayer, J. Electrochem. Soc. **122**, 651 (1975).
[5]H.R. Pettit and G.R. Booker, Inst. Phys. Conf. Ser. No **10**, 290 (1971).
[6]K.B. Winterbon, *Ion Implantation Range and Energy Deposition Distributions*, Vol. 2, *Low Incident Ion Energies*, (Plenum, New York, 1975).
[7]W.K Hofker, D.P. Oosthock, N.J. Koeman, and H.A.M. De Grefte, Radiat. Eff. **24**, 223 (1975).
[8]M.N. Kamalov, L.I. Kolesnik, M.G. Mil'vidskiî, V.V. Rakov, and I.N. Shershakova, Sov. Phys. Semicond. **12**, 340 (1978).
[9]C.A. Evans, Jr., V.R. Deline, T.W. Sigmon, and A. Lidow, Appl. Phys. Lett. **35**, 291 (1979).
[10]D.K. Sadana and G.R. Booker, Radiat. Eff. **42**, 35 (1979).
[11]S.S. Kular, B.J. Sealy, K.G. Stephen, D.K. Sadana, and G.R. Booker (unpublished).
[12]L.H. Skolnik, W.G. Spitzer, A. Kahan, F. Euler, and R.G. Hunsperger, J. Appl. Phys. **43**, 2146 (1972).
[13]D.L. Kendall, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1968), Vol. 4, p. 177.
[14]F.A. Kröger, *The Chemistry of Imperfect Crystals* (Wiley, New York, 1964), p. 703.

dc bias dependence of W-Ni and W-Co point-contact diodes as harmonic generators and mixers at 9.4 μm

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The S/N ratios of the rf beat notes between harmonics of an x-band microwave source and the mixed output of two CO_2 lasers at different frequencies are studied by means of the W-Ni and W-Co point-contact diodes at various mixing orders and various conditions of dc bias voltage. By applying the appropriate dc bias voltage to the W-Co diode in the even mixing orders, improvements on the S/N ratios by 5–10 dB are obtained.

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The metal-insulator-metal (MIM) point-contact diodes as harmonic generators and mixers of submillimeter and infrared laser radiation have been used extensively over the past decade for frequency measurements.[1-3] The useful properties of MIM diodes, which consist of sharply tipped tungsten wires contacting metal posts arise from their nonlinear current-voltage characteristics due to the electron tunneling effect,[4] with the tungsten wire functioning as a traveling-wave antenna.[5,6]

Sanchez *et al.* have experimentally suggested that a dc bias voltage increases the intensity of the beat signal for the even mixing order in the W-Ni diode.[7] Faris and Gustafson have analyzed harmonic mixing characteristics of MIM diodes under applied dc bias voltages.[8] Kramer previously re-

